

# IRON-BASE SINTERED ALLOY MATERIAL FOR VALVE SHEET AND PROCESS FOR PREPARING THE SAME

## Background of the Invention

### Field of the Invention

The present invention relates to a sintered alloy material, in particular, an iron-base sintered alloy material which is suitable for a valve sheet for an internal combustion engine.

### Related Art Statement

A valve sheet plays a roll of sealing a combustion gas and cooling a valve, and is used as press-fitting into a cylinder-head of an engine. A valve sheet is required to have a low opposite aggressibility so as not to wear a counterpart valve, in addition to the excellent heat resistance, abrasion resistance and corrosion resistance.

Recently, in an automobile engine, there are increased demands on improvement in long life, high output, cleaning of exhaust gas, increase in fuel efficiency and the like. For this reason, a valve sheet for an automobile engine is also required to endure the severer environment in use than ever, and it has become necessary to further improve the heat resistance and the abrasion resistance.

In response to such the demand, for example, JP-A No. 2000-54087 proposes an iron-base sintered alloy material for a valve sheet in which a Cr-Mo-Si-Co type alloy particle as a hard particle is dispersed in a base matrix phase at an area ratio of 10 to 30%, and a porosity is 1 to 10% by volume ratio. This iron-base sintered alloy material for a valve sheet is prepared by a process comprising a molding step of filling a raw material powder into a mold, and compressing and molding the powder to obtain a green compact, a primary sintering step of heating and sintering the green compact to a temperature range of 900 to 1200°C in the protective atmosphere to obtain a

primary sintered body, a re-pressing/forging step of re-pressing or forging the primary sintered body to obtain a re-pressed compact or forged compact having a high density, and a secondary sintering step of sintering the re-pressed compact or the forged compact at a temperature range of 1000 to 1200°C in the protective atmosphere. According to the technique described in this gazette, a sintered body having a high density is obtained, and an iron-base sintered alloy material having the improved high temperature strength and thermal conductivity is obtained.

In addition, JP-A No. 2000-160307 describes a process for preparing a powder metallurgy part which is suitable for a valve sheet insert, in which a mixture containing 15 to 30 wt% of a valve steel powder, 0 to 10 mass% of Ni powder, 0 to 5 mass% Cu powder, 5 to 15 mass% of a ferroalloy powder, 0 to 15 mass% of a tool steel powder, 0.5 to 5 mass% of a solid lubricant, 0.5 to 2.0 mass% of graphite, 0.3 to 1.0 mass% of a temporary sliding agent, and substantially a low alloy steel powder as the balance is compression-molded by press to an unprocessed density in a range of 6.7 to 7.0 g/cm<sup>3</sup>, preferably density of 6.8 to 7.0 g/cm<sup>3</sup>, most preferably 6.9 g/cm<sup>3</sup> to obtain an at least generally net-like shaped material, followed by sintering. According to the technique described in this gazette, a powder metallurgy part having a relatively high density is obtained even by one-stage pressing and sintering method, and the part has the excellent abrasion resistance, the excellent high-temperature resistance, the high creep strength and the high fatigue strength, and is further improved in the corrosion resistance, and is also improved in the mechanical processability.

However, according to the technique described in JP-A No. 2000-54087, in order to obtain a high density sintered body having a porosity of 1 to 10%, a re-pressing/forging step and further a secondary sintering step of a sintered body are necessary and, thus, there is a problem that steps become complicated and the product cost is increased. According to the technique described in JP-A No. 2000-160307, a relatively high density is obtained by a

one-stage molding and one-stage sintering method. However, in order to obtain a high density, a difficult step is required, and, thus, there is a problem that the product cost is increased.

Recently, from a viewpoint of earth environmental conservation, a gasoline engine (internal combustion engine) is strongly required to enhance the fuel efficiency. For this reason, while an air-fuel ratio (A/F value) of a mixed gas for the conventional internal combustion engine is about 10, a gasoline engine is worked by setting the A/F value at high as about 12. As a result, there are problems that the cooling effect due to a gasoline at working of an internal combustion engine is lowered, a maximum burning temperature becomes very high due to approaching a theoretical air-fuel ratio, and a thermal load applied to a valve sheet is remarkably increased.

In addition, when the A/F value of a mixed gas in a gasoline engine becomes high, there is a problem that a combustion gas becomes cleaner than ever, adhesion of the combustion product which is said to have the effect on lubrication of a valve and a valve sheet, and the abrasion resistance is lowered.

Further, with a change in such the combustion circumstance in a gasoline engine, iron oxide produced on the surface of a valve and a valve sheet is decreased than ever and, for this reason, there is a problem that adhesive wear is easily caused, and a valve and a valve sheet are remarkably worn.

### Summary of the Invention

- (1) An iron-base sintered alloy material in which a hard particle is dispersed in a base matrix phase, and which is used for a valve sheet, characterized in that the hard particle is dispersed at 5 to 40% by area ratio, a porosity is 12 to 55% by volume ratio, and a density after sintering is 6.1 to 6.9 g/cm<sup>3</sup>.
- (2) An iron-base sintered alloy material, wherein the composition of a base matrix portion consisting of the base matrix phase and the hard particle has a

composition containing a total of 10.0 to 40.0% of one or more selected from Ni: 2.0 to 23.0%, Cr: 0.4 to 15.0%, Mo: 3.2 to 15.0%, Cu: 0.2 to 3.0%, Co: 3.0 to 15.0%, V: 0.1 to 0.5%, Mn: 0.1 to 0.5%, W: 0.2 to 6.0%, C: 0.8 to 2.0%, Si: 0.1 to 1.0% and S: 0.1 to 1.0% by mass, and the balance substantially comprising Fe, the hard particle is a particle composed of one or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe in (1).

(3) The iron-base sintered alloy material, wherein a solid lubricant particle is further dispersed in the base matrix phase at an area rate of 0.3 to 3.5% in (1) or (2).

(4) The iron-base sintered alloy material, wherein the solid lubricant particle is one or more selected from a sulfides and a fluoride in (3).

(5) A process for preparing an iron-base sintered alloy material for a valve sheet, which comprises successively performing a molding step of filling into a mold a raw material powder obtained by blending and mixing 20 to 70% of pure iron powder, 10 to 50% of an alloy iron powder containing a total of 3 to 30% of one or more selected from C, Ni, Cr, Mo, Cu, Co, W, V and Mn and the balance substantially Fe, and 5 to 40% of a hard particle powder composed of one or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe by mass relative to a total amount of the raw material powder, and compressing and molding the raw material powder by adjusting the compressing and molding conditions to obtain a green compact having a predetermined green density, and a sintering step of adjusting the sintering conditions to heat and sinter the green compact in the protective atmosphere to obtain a sintered body, whereby a sintered body having a density after sintering of 6.1 to 6.9 g/cm<sup>3</sup> and a porosity of 12 to 25% by volume ratio is obtained.

(6) The process for preparing an iron-base sintered alloy material for a valve sheet, wherein a solid lubricant particle powder is further blended in the raw material powder at 0.2 to 3.0 parts by weight relative to a total amount of 100 parts by weight of the raw material powder in (5).

(7) The process for preparing an iron-base sintered alloy material for a valve

sheet, wherein an alloy element powder of one or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C is blended, in place of a part or all of the alloy iron powder, at 0.3 to 15% by mass relative to a total amount of the raw material powder in (5) or (6).

(8) The process for preparing an iron-base sintered alloy material for a valve sheet, wherein the predetermined green density is 6.2 to 7.0 g/cm<sup>3</sup> in any one of (5) to (7).

(9) The process for preparing an iron-base sintered alloy material for a valve sheet, wherein the sintering conditions are conditions under which sintering is performed by heating to a temperature range of 1000 to 1200°C in any one of (5) to (8).

(10) A valve sheet made of an iron-base sintered alloy, which comprises, as a material, the iron-base sintered alloy material for a valve sheet according to any one of (1) to (4).

#### Brief Description of the Drawings

Fig. 1 shows the optical micrographic structure of an iron-base sintered alloy material of Example (test No. 2) of the present invention.

Fig. 2 shows a schematic view of Fig. 1.

Fig. 3 shows the optical micrographic structure of an iron-base sintered alloy material of Example (test No. 5) of the present invention.

Fig. 4 shows a schematic view of Fig. 3.

Fig. 5 shows the optical micrographic structure of an iron-base sintered alloy material of Comparative Example (test No. 14).

Fig. 6 shows a schematic view of Fig. 5.

Fig. 7 shows a schematic view for explaining a single body rig abrasion tester.

#### Detailed Description of the Preferred Embodiments

An object of the present invention is to advantageously solve the

aforementioned prior art problems, and provide an iron-base sintered alloy material for a valve sheet which is particularly suitable for recent gasoline engine (internal combustion engine) using a mixed gas having a high A/F value, which has the high temperature strength, the creep strength and the fatigue strength, and also has the excellent abrasion resistance, the excellent iron oxide producing property, and a process for preparing the same.

In order to attain the above object, the present inventors intensively studied factors influencing on improvement of the abrasion resistance of a valve sheet. As a result, the present inventors found that, under the operating environment of the aforementioned recent internal combustion engine, in particular, a gasoline engine (internal combustion engine) in which an A/F value is set high, an amount of iron oxide produced on a sliding contact surface of a valve sheet by thermal load during operation of an internal combustion engine has the great influence on the abrasion resistance of a valve and a valve sheet. Since a highly densified valve sheet has a small porosity, an amount of iron oxide produced on the sliding contact surface of a valve sheet becomes further small, adhesion wear is easily caused, and abrasion of a valve and a valve sheet becomes more remarkable. In addition, according to the study of the present inventors, it was found that the mechanical strength dependent on a sintered density has little influence on the abrasion resistance.

From the foregoing, the present inventors found that, by maintaining the tensile strength, the creep strength, the fatigue strength and the like without increasing a sintered density and, under such the situation, molding a raw material powder into a molded green compact having a relatively low density, sintering the compact to adjust a sintered density relatively low and a porosity in an appropriate range, and making relatively many fine pores present in a sintered body, production of iron oxide due to thermal load at operation of an internal combustion engine is accelerated, and the compatibility between a valve and valve sheet is improved and, as a result, the

abrasion resistance is improved.

Based on the above findings, we further studied, which resulted in completion of the present invention.

The iron-base sintered alloy material for a valve sheet of the present invention is a sintered body comprising a base matrix phase, a hard particle dispersed in the base matrix phase, or further a solid lubricant particle dispersed in the base matrix phase, and pores.

It is preferable that the composition of a base matrix portion containing a base matrix phase and a hard particle has a composition containing a total of 10.0 to 40.0% of one or more selected from Ni: 2.0 to 23.0%, Cr: 0.4 to 15.0%, Mo: 3.2 to 15.0%, Cu: 0.2 to 3.0%, Co: 3.0 to 15.0%, V: 0.1 to 0.5%, Mn: 0.1 to 0.5%, W: 0.2 to 6.0%, C: 0.8 to 2.0%, Si: 0.1 to 1.0% and S: 0.1 to 1.0% by mass, and the balance substantially Fe.

Ni, Cr, Mo, Cu, Co, V, Mn, W, C, Si and S are all contained in a base matrix phase and a hard particle, are elements for improving the abrasion resistance, and can be contained at a total of 10.0 to 40.0% by mass by selecting one or more.

Ni is an element for increasing the hardness and the heat resistance in addition to the abrasion resistance, and such the effect is recognized when Ni is contained at 2.0% by mass or more. On the other hand, when Ni is contained at an amount larger than 23.0% by mass, the opposite aggressibility is increased. Preferably, Ni is contained at 5.0% by mass or more.

Cr is contained in a base matrix phase and a hard particle, and is an element for increasing the hardness and the heat resistance in addition to the abrasion resistance, and such the effect is recognized when Cr is contained at 0.4% by mass or more. On the other hand, when Cr is contained at an amount larger than 15.0% by mass, the opposite aggressibility is increased. The amount of Cr is preferable in a range of from 3.0 to 10.0% by mass.

Mo is contained in a base matrix phase and a hard particle, and is an element for increasing the hardness and the heat resistance in addition to the

abrasion resistance, and such the effect is recognized when Mo is contained at 3.2% by mass or more. On the other hand, when Mo is contained at an amount larger than 15.0% by mass, the opposite aggressibility is increased.

Cu is an element for reinforcing a base matrix phase and increasing the hardness in addition to the abrasion resistance, and the above effect is recognized when Cu is contained at 0.2% by mass or more. On the other hand, when Cu is contained at an amount larger than 3.0% by mass, the opposite aggressibility is increased.

Co is an element which has the action of improving the abrasion resistance, additionally, of reinforcing binding between a hard particle and a base matrix phase, and further has the action of improving the heat resistance, and the above effect is recognized when Co is contained at 3.0% by mass or more. On the other hand, when Co is contained at an amount larger than 15.0% by mass, the opposite aggressibility is increased.

V is an element for reinforcing a base matrix phase, improving the abrasion resistance and, additionally, increasing the hardness, and the above effect is recognized when V is contained at 0.1% by mass or more. On the other hand, when V is contained at an amount larger than 0.5% by mass, the opposite aggressibility is increased.

Mn is an element for reinforcing a base matrix phase, improving the abrasion resistance and, additionally, increasing the hardness, and the above effect is recognized when Mn is contained at 0.1% by mass or more. On the other hand, when Mn is contained at an amount larger than 0.5% by mass, the opposite aggressibility is increased.

W is an element for reinforcing a base matrix phase, improving the abrasion resistance, and additionally, increasing the hardness, and above effect is recognized when W is contained at 0.2% by mass or more. On the other hand, when W is contained at an amount larger than 6.0% by mass, opposite aggressibility is increased.

C is an element for improving the abrasion resistance and,



additionally, reinforcing a base matrix phase and improving the sintering diffusibility, and above effect is recognized when C is contained at 0.8% by mass or more. On the other hand, when C is contained at an amount larger than 2.0% by mass, the opposite aggressibility is increased.

Si and S are elements for improving the abrasion resistance and, additionally, increasing the strength of a base matrix phase, and the above effect is recognized when Si is contained at 0.1% by mass or more, and when S is contained at 0.1% by mass or more, respectively. On the other hand, when Si is contained at an amount larger than 1.0% by mass, or when S is contained at an amount larger than 1.0% by mass, the opposite aggressibility is increased.

In addition, when a total content of the aforementioned components is less than 10.0% by mass, the hardness of the base matrix phase, and the high temperature properties such as the high temperature strength and the creep strength are decreased. On the other hand, when the total content is larger than 40.0% by mass, the opposite aggressibility is increased. For this reason, in the present invention, it is preferable that the total content of the aforementioned components is limited to a range of 10.0 to 40.0% by mass.

In a base matrix portion, the balance other than the aforementioned components is substantially Fe.

In addition, a hard particle dispersed in a base matrix phase makes a contribution to improvement in the abrasion resistance, and its dispersion amount is 5.0 to 40.0% by area ratio in the present invention. When an area ratio of a hard particle is 5.0% or more, the above-mentioned effect can be expected. On the other hand, a hard particle is dispersed at an area ratio larger than 40.0%, the opposite aggressibility is increased. For this reason, in the present invention, an area ratio of hard particle is limited to 5.0 to 40.0%. Preferably, an area ratio is 10.0 to 30.0%.

It is preferable that a hard particle to be dispersed in the base matrix phase is a particle comprising one or more elements selected from C, Cr, Mo,

Co, Si, Ni, S and Fe. It is preferable that a hard particle has the aforementioned composition and, further, has the hardness in a range of Hv 600 to 1200. When the hardness of a hard particle is less than Hv 600, the abrasion resistance is decreased. On the other hand, when the hardness exceeds Hv1200, the toughness is decreased, and a risk of occurrence of chipping and cracking of a valve sheet is increased.

Examples of such the hard particle include a Cr-Mo-Co type intermetallic compound particle, a Ni-Cr-Mo-Co type intermetallic compound particle, a Fe-Mo alloy particle, a Fe-Ni-Mo-S type alloy particle and a Fe-Mo-Si alloy particle.

The Cr-Mo-Co type intermetallic compound particle is an intermetallic compound comprising 5.0 to 20.0% of Cr and 10.0 to 30.0% of Mo by mass, and the balance substantially Co. The Ni-Cr-Mo-Co type intermetallic compound particle is an intermetallic compound comprising 5.0 to 20.0% of Ni, 15.0 to 30.0% of Cr, 17.0 to 35.0% of Mo by mass, and the balance substantially Co. The Fe-Mo alloy particle is an alloy particle comprising 50.0 to 70.0% of Mo by mass and the balance substantially Fe. The Fe-Ni-Mo-S type alloy particle is an alloy particle comprising 50.0 to 70.0% of Ni, 20.0 to 40.0% of Mo, 1.0 to 5.0% of S by mass, and the balance substantially Fe. The Fe-Mo-Si alloy particle is an alloy particle comprising 5.0 to 20.0% of Si, 20.0 to 40.0% of Mo by mass, and the balance substantially Fe.

In addition, in the present invention, a solid lubricant particle may be dispersed in a base matrix phase in addition to the hard particle. The solid lubricant particle has the effect of improving the machinability and the abrasion resistance, and decreasing the opposite aggressibility. As the solid lubricant particle, one or more selected from sulfides such as MnS and MoS<sub>2</sub> and fluorides such as CaF<sub>2</sub>, and a mixture thereof are preferable. It is preferable that the solid lubricant particle is dispersed at a total of 0.3 to 3.5% by area ratio. When an amount of solid lubricant particle is less than 0.3%,

the amount of the solid lubricant particle is too small, the machinability is deteriorated, occurrence of adhesion is accelerated, and the abrasion resistance is decreased. On the other hand, even when the solid lubricant particle is dispersed at an amount larger than 3.5%, the effect becomes saturated, the effect corresponding to the amount can not be expected. For this reason, it is preferable that an area ratio of the solid lubricant particle is limited to 0.3 to 3.5%.

In addition, the iron-base sintered alloy material for a valve sheet of the present invention has a porosity of 12 to 25% by volume ratio. The presence of a pore influences on the high temperature strength, the fatigue strength and the thermal conductivity. When a porosity is less than 12% by volume ratio, production of iron oxide effective for the abrasion resistance becomes insufficient at operation of an internal combustion engine using a mixed gas having a high A/F value. On the other hand, when a porosity is larger than 25%, decrease of the strength such as the room temperature strength, the high temperature strength and the like becomes remarkable. For this reason, in the present invention, a porosity is limited to 12 to 25% by volume ratio. As a porosity referred in the present invention, a value measured by an image analyzing method is used.

In addition, the iron-base sintered alloy material for a valve sheet of the present invention has a density after sintering of 6.1 to 6.9 g/cm<sup>3</sup>. The density after sintering influences on the high temperature strength, the fatigue strength, and the thermal conductivity. When the density after sintering is less than 6.1 g/cm<sup>3</sup>, decrease of these strength and thermal conductivity is remarkable. On the other hand, when the density exceeds 6.9 g/cm<sup>3</sup>, in particular, when an internal combustion engine using a mixed gas having a high A/F value is operated, production of iron oxide effective for the abrasion resistance becomes insufficient and, moreover, steps become complicated due to increase in a density, leading to a rise of the manufacturing cost. For this reason, in the present invention, the density after sintering is

limited to a range of 6.1 to 6.9 g/cm<sup>3</sup>.

It is preferable that the microstructure of a base matrix phase is composed of 30 to 60% of a pearlite phase and 40 to 70% of a high alloy diffusion phase, by area ratio relative to an area of a base matrix phase as 100 %, excluding these of the hard particles and further solid lubricant particles, if any.

In order to obtain the iron-base sintered alloy material of the present invention, first, to be the above-mentioned composition of base matrix portion containing the base matrix phase and the hard particle, 20 to 70% of a pure iron powder, 10 to 50% of an alloy iron powder containing a total of 3 to 30% of one or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C, and the balance substantially Fe, and 5 to 40% of a hard particle powder composed of one or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe by mass relative to a total amount of a raw material powder, that is a total amount of pure iron powder, alloy iron powder, and hard particle powder, or further 0.2 to 3.0 parts by weight of a solid lubricant powder relative to 100 parts by weight of a total amount of a raw material powder, are blended, and are kneaded to obtain a mixed powder. In addition, as a lubricant, zinc stearate or the like may be further added.

When a blending amount of a pure iron powder to be blended as a raw material powder is less than 20% by mass, an amount of production of iron oxide effective for improvement in the abrasion resistance is decreased, and the abrasion resistance is deteriorated. On the other hand, when the amount of the pure iron powder is larger than 70% by mass, an amount of produced iron oxide becomes larger, but the hardness of a base matrix phase is decreased, and the abrasion resistance is deteriorated at an operation initial stage before production of iron oxide.

An alloy iron powder is blended in order to increase the hardness and the high temperature strength of a base matrix phase. When an amount of an alloy iron powder to be blended is less than 10%, the aforementioned effect

is deficient. On the other hand, when the amount is larger than 50%, the above mentioned effect becomes saturated, and the effect corresponding to an blended amount can not be expected, being economically disadvantageous. An alloy iron powder contains a total of 3 to 30% by mass of one or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C, and the balance substantially Fe. When the content of one or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C in an alloy iron powder is less than a total of 3% by mass, the effect of blending of the aforementioned alloy iron powder is not perceived. On the other hand, when the above-mentioned alloy elements are contained in an alloy iron powder at a total amount larger than 30% by mass, the aforementioned effect becomes saturated, and the effect corresponding to an blending amount can not be obtained, being economically disadvantageous.

A hard particle powder composed of one or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe is blended from a viewpoint of improvement in the abrasion resistance. When an blending amount thereof is less than 5% by mass relative to a total amount of a raw material powder, the aforementioned effect can not be expected. On the other hand, when the powder is blended at an amount larger than 40%, the opposite aggressibility is increased.

In addition, a solid lubricant particle powder is blended as necessary in order to improve the machinability and the abrasion resistance, and decrease the opposite aggressibility. When an blending amount is less than 0.2 parts by mass relative to 100 parts by mass of a total amount of a raw material powder, which is total amount of pure iron powder, alloy iron powder and a hard particle powder, the machinability is deteriorated, and the abrasion resistance is reduced. On the other hand, when the powder is blended at an amount larger than 3.0 parts by mass, the effect becomes saturated, and the effect corresponding to the amount can not be obtained.

In addition, in the present invention, it is preferable that, in place of a part or all of the aforementioned alloy iron powder, an alloy element powder of

one or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C is blended at 0.3 to 15% by mass relative to a total amount of a raw material powder which is a total amount of pure iron powder, alloy iron powder, alloy element powder, and hard particle powder. Ni, Cr, Mo, Cu, Co, V, Mn, W and C powders can be all blended by selection in place of an alloy iron powder, in order to increase the hardness and the high temperature strength of a base matrix base. When a total blending amount of these alloy element powders is less than 0.3 % by mass, the hardness and the high temperature strength of the base matrix phase are low, and the abrasion resistance is reduced. On the other hand, even when those powders are blended at an amount larger than 15% by mass, the effect becomes saturated, and the effect corresponding to the amount can not be obtained.

It is preferable that the aforementioned pure iron powder, alloy iron powder, alloy element powder and hard particle powder, or further a solid lubricant powder are blended at a predetermined amount, and mixed and kneaded to obtain a mixed powder.

In the present invention, an iron-base sintered alloy material for a valve sheet is obtained via a molding step of filling the mixed powder into a mold, and compress molding the mixed powder by a molding press or the like to obtain a green compact, and a sintering step of heating and sintering the green compact in the protective atmosphere such as ammonia degrading gas or the like, to obtain a sintered body. As the sintering condition, it is preferable to heat the green compact at a temperature range of 1000 to 1200°C.

In the present invention, it is preferable to adjust the press molding conditions in a molding step and the sintering body in a sintering step so that a density after sintering of a sintered body becomes 6.1 to 6.9 g/cm<sup>3</sup> and a porosity becomes 12 to 25% by volume ratio. It is preferable from a viewpoint of control of a density after sintering that, in a molding step, the press molding conditions are adjusted so that a density of a green compact becomes 6.2 to 7.0

g/cm<sup>3</sup>.

The resulting sintered body of iron-base sintered alloy material is subjected to cutting and grinding processes to obtain a valve sheet having desired size and shape.

### Examples

As a raw material powder, kinds shown in Table 1 of an alloy iron powder or alloy element powder, a hard particle powder, or further a solid lubricant powder were blended into pure iron powder at amounts shown in Table 1, and the materials were mixed and kneaded to obtain a mixed powder. An blending amount of each raw material powder is expressed as % by mass relative to a total amount of (pure iron powder + alloy iron powder or alloy element powder + hard particle powder). An amount of a solid lubricant powder to be blended is expressed as parts by weight relative to 100 parts by weight of a total amount of a raw material powder, which is a total amount of the pure iron powder, the alloy iron powder or the alloy element powder, and the hard particle powder.

Then, the mixed powder was filled into a mold, and compressed and molded by a molding press to obtain a green compact. The conditions of compressing and molding were changed to adjust a density of a green compact.

Then, the green compact was subjected to a sintering step of sintering for 10 to 30 minutes in the protected atmosphere of ammonia degrading gas at 1000°C to 1200°C and was obtained a sintered body of iron-base sintered alloy material.

A test sample was collected from the resulting sintered body, and the composition of a base matrix portion, a porosity of a sintered body, and a density after sintering were measured. Aporosity was measured by an image analyzing method. A density was measured by an Archimedes method.

From the resulting sintered body, a valve sheet (size and shape:  $\phi$

33mm ×  $\phi$  29mm × 6.0mm) was manufactured by a cutting process and a grinding process, and a single body rig abrasion test, which is abrasion resistance confirming test, and an oxidation test, which is iron oxide production amount confirming test, were performed.

(1) Single body rig abrasion test (abrasion resistance confirming test)

A single body rig abrasion test was performed using a single body rig abrasion tester shown in Fig. 4. After a valve sheet 1 was press-fitted in a device 2 corresponding to a cylinder head, a valve 4 was moved up and down repeatedly by the crank mechanism while heating a valve 4 and a valve sheet 1 by a heat source (LPG + Air) 3 attached to the tester, and a abrasion amount was measured by a valve sinking amount. The test conditions are as follows:

Test temperature: 400°C (sheet surface)

Test time: 9.0 hr

Cam rotation speed: 3000 rpm

Valve rotation speed: 20 rpm

Spring load: 35 kgf (345N) ( at setting )

Valve material: SUH35

Lift amount: 9.0 mm

(2) Oxidation test (iron oxide production amount confirming test)

After a valve sheet was degreased and cleaned, it was charged into a heating furnace, and heat-treated under the following test conditions:

Heating temperature: 300, 400, 500°C

Heating time: 2h

Heating atmosphere: in the air,

weights of the valve sheet before and after thermal treatment were measured, and an amount increased by oxidation was obtained. An amount increased by oxidation (%) was calculated by [ {(weight after heat treatment) - (weight before heat treatment) } / (weight before heat treatment) ] × 100 (%).

The resultant results are shown in Table 2.

In Examples of the present invention (test No. 1 to No. 12, No. 19 to



No. 22), abrasion amounts of a valve sheet are 10 to 17  $\mu\text{m}$ , abrasion amounts of valve are 7 to 13  $\mu\text{m}$ , an amount increased by oxidation in each test temperature is large, and an iron-base sintered alloy material satisfying the excellent abrasion resistance and the excellent iron oxide production property at the same time is obtained. On the other hand, in Comparative Examples outside the scope of the present invention (test No. 13 to No. 18), abrasion amounts of a valve sheet are 28 to 56  $\mu\text{m}$ , and abrasion amounts of a valve are 25 to 58  $\mu\text{m}$  and, as compared with Example of the present invention, the abrasion resistance is reduced, the opposite aggressibility is increased, and an amount increased by oxidation is not always increased and, thus, the excellent abrasion resistance and the excellent iron oxide production property are not satisfied at the same time. In particular, in a test No. 13 (Comparative Example) having a high density after sintering, a valve and a valve sheet have greater abrasion amounts than those of Examples of the present invention. In a test No. 14 (Comparative Example) having a high porosity and a small density after sintering, in particular, a abrasion amount of a valve sheet is high.

One example of the microstructure of the resulting iron-base sintered alloy material is shown in Fig. 1, Fig. 3 and Fig. 5.

Fig. 1 shows the optical micrographic structure of a base part in a test No. 2 (Example of present invention), and Fig. 2 is a schematic view of Fig. 1. A base matrix portion has a hard particle (H) and a solid lubricant part dispersed in a base matrix phase. The structure of a base matrix phase is composed of pearlite (P) and high alloy diffusion phase (R). V is a pore.

Fig. 3 shows the optical micrographic structure of a base matrix portion in a test No. 5 (Example of present invention), and Fig. 4 is a schematic view of Fig. 3.

Fig. 5 is the optical micrographic structure of a base part in a test No. 14 (Comparative Example), and Fig. 6 is a schematic view of Fig. 5.

The present invention is not limited by the aforementioned Examples.

According to the present invention, an iron-base sintered alloy material has the excellent abrasion resistant and the high iron oxide production property. And this material as an automobile valve sheet shows the excellent durability to severe operation of a engine setting a high A/F value, exerting the especial industrial effect.

Table 1

Test No.	Raw material powder blending amount (% by mass)							Solid lubricant powder		Green compact
	Pure iron powder	Alloy iron powder		Alloy element powder		Hard particle powder		Kind'''	Blending amount (parts by weight relative to 100 parts by weight of raw material powder)	Density g/cm³
		Kind'	Blending amount	Kind: Blending amount	Total of blending amount	Kind''	Blending amount''			
1	40.0	C	45.0	C:1.0	1.0	d	14.0	(B)	1.0	6.70
2	42.9	B	45.0	C:1.1	1.1	a	11.0	(A)	0.5	6.70
3	68.8	-	-	C:1.2, Ni:5.0, Co:5.0	11.2	b	20.0	(A)	0.5	6.60
4	63.8	-	-	C:1.2, Ni:6.0, Co:4.0, Mo:3.0	14.2	b	22.0	(B)	1.0	6.55
5	40.9	A	40.0	C:1.1	1.1	c	18.0	(A)	2.0	6.55
6	65.8	-	-	C:1.2, Ni:6.0, Co:4.0, Cu:3.0	14.2	c	20.0	(B)	2.0	6.45
7	22.0	D	45.0	C:1.0	1.0	d	32.0	(B)	1.0	6.50
8	64.8	E	14.0	C:1.2	1.2	d	20.0	(B)	1.0	6.45
9	65.0	F	12.0	C:1.0	1.0	a	22.0	(A)	0.5	6.40
10	38.7	B	40.0	C:1.3	1.3	a	20.0	(A)	1.5	6.20
11	64.8	-	-	C:1.2, Ni:6.0, Co:3.0	10.2	b	25.0	(A)	1.0	6.15
12	60.7	-	-	C:1.3, Ni:6.0, Co:4.0, Cu:3.0	14.3	c	25.0	(B)	1.0	6.15
13	39.8	C	45.0	C:1.2	1.2	d	14.0	(B)	1.0	7.05
14	38.0	E	40.0	C:2.0	2.0	a	20.0	(A)	1.5	6.10
15	14.7	F	60.0	C:1.3	1.3	d	24.0	(B)	0.5	6.50
16	90.1	A	5.0	C:0.9	0.9	b	4.0	-	-	6.50
17	17.4	B	31.5	C:1.1	1.1	d	50.0	(B)	2.5	6.20
18	83.7	-	-	C:1.1, Ni:0.2	1.3	b	15.0	(A)	0.3	6.00
19	40.0	C	45.0	C:1.0	1.0	d	14.0	(B)	1.0	6.85
20	40.0	C	45.0	C:1.0	1.0	d	14.0	(B)	1.0	7.00
21	61.0	C	20.0	C:1.0	1.0	b	18.0	(A)	0.5	6.86
22	68.8	E	10.0	C:1.2	1.2	d	20.0	(B)	1.0	6.75

\*) Alloy iron powder;

A: 1.0Cr-0.5Mn-0.3 Mo-bal.Fe  
 B: 3.0Cr-0.2Mo-bal.Fe  
 C: 4.0Ni-1.5Cu-0.5Mo-bal.Fe  
 D: 1.5C-12Cr-1Mo-1V-bal.Fe (SKD11)  
 E: 0.8C-4Cr-5Mo-2V-6W-bal.Fe (SKH51)  
 F: 1.2C-4Cr-3Mo-10W-3V-10Co-bal.Fe (SKH57)

\*\*\*) Solid lubricant particle powder;

(A): MnS  
 (B): CaF<sub>2</sub>

\*\*) Hard particle powder;

a: Cr-Mo-Co type intermetallic compound (Hv: 700)  
 b: Ni-Cr-Mo-Co type intermetallic compound (Hv: 1100)  
 c: Fe-Mo type hard particle (Hv: 1100)  
 d: Fe-Ni-Mo-S type hard particle (Hv: 600)

Table 2

Test No.	Sintered body													Test results				Note		
	Base matrix portion composition (% by mass)													Single rig test					Oxidation test	
	C	Ni	Cr	Mo	Cu	Co	Others	Total amount of alloy element	Balance	Hard particle Area %	Solid lubricant particle Area %	Porosity Volume %	Density after sintering g/cm <sup>3</sup>	Abrasion amount (μm)		Amount increased by oxidation (%)				
														Sheet	Valve	300°C	400°C		500°C	
1	1.0	11.0	-	4.0	0.7	-	Si:0.1, S:0.4	17.2	Fe	12.0	1.2	16.5	6.60	14	7	0.21	0.58	0.74	Example of present invention	
2	1.1	-	2.3	3.2	-	6.6	V:0.1, Si:0.3	13.6	Fe	10.0	0.7	17.0	6.58	16	8	0.26	0.58	0.76	Example of present invention	
3	1.2	7.0	4.8	4.8	-	13.0	Si:0.4	31.2	Fe	18.0	0.7	17.0	6.55	14	11	0.30	0.60	0.81	Example of present invention	
4	1.2	8.2	5.3	8.3	-	12.8	Si:0.4	36.2	Fe	20.0	1.2	19.0	6.48	12	10	0.32	0.65	0.87	Example of present invention	
5	1.1	-	0.4	10.1	-	-	Mn:0.3	11.9	Fe	16.0	2.3	20.0	6.45	13	7	0.24	0.52	0.73	Example of present invention	
6	1.2	6.0	-	12.0	3.0	4.0	-	26.2	Fe	18.0	2.3	20.5	6.40	11	10	0.30	0.64	0.84	Example of present invention	
7	1.7	21.1	5.4	9.4	-	-	V:0.4, Si:0.2, S:0.9	39.1	Fe	30.0	1.2	20.2	6.45	10	13	0.18	0.52	0.67	Example of present invention	
8	1.3	13.2	0.6	6.3	-	-	V:0.3, W:0.8, Si:0.2, S:0.5	23.2	Fe	18.0	1.2	20.5	6.40	17	9	0.27	0.61	0.81	Example of present invention	
9	1.15	-	2.4	6.7	-	14.3	V:0.4, W:1.1, Si:0.6	26.7	Fe	20.0	0.7	21.5	6.35	13	10	0.30	0.64	0.83	Example of present invention	
10	1.3	-	2.9	5.8	-	12.0	V:0.1, S:0.5	22.6	Fe	18.0	1.7	23.5	6.15	12	9	0.28	0.62	0.87	Example of present invention	
11	1.2	8.5	6.0	6.0	-	13.0	Si:0.5	35.2	Fe	23.0	1.2	24.0	6.12	10	8	0.33	0.71	0.97	Example of present invention	
12	1.3	6.0	-	15.0	3.0	4.0	-	29.3	Fe	23.0	1.2	24.0	6.10	11	10	0.29	0.73	0.97	Example of present invention	
13	1.2	11.0	-	4.2	0.7	-	Si:0.1, S:0.4	17.6	Fe	12.0	1.2	10.0	7.01	35	25	0.01	0.05	0.13	Comparative Example	
14	2.4	-	3.3	7.7	-	12.0	V:0.8, Mn:0.1, W:2.3, Si:0.6	29.2	Fe	18.0	1.7	30.5	6.02	52	26	0.25	0.73	0.96	Comparative Example	
15	2.0	15.8	2.5	8.9	-	5.6	V:2.0, Si:0.3, S:0.6, W:5.5	43.2	Fe	22.0	0.7	20.0	6.47	44	38	0.02	0.07	0.14	Comparative Example	
16	0.9	0.4	1.0	1.0	-	1.6	Si:0.1	5.0	Fe	3.0	-	20.5	6.45	56	25	0.21	0.68	0.88	Comparative Example	
17	1.1	33.0	1.0	14.1	-	-	V:0.1, Si:0.4, S:1.4	51.1	Fe	45.0	3.0	24.0	6.15	28	58	0.20	0.72	0.87	Comparative Example	
18	1.1	1.7	3.6	3.6	-	6.0	Si:0.3	16.3	Fe	13.0	0.5	25.5	6.00	54	28	0.29	0.73	0.93	Comparative Example	
19	1.0	11.0	-	4.2	0.7	-	Si:0.1, S:0.4	17.4	Fe	12.0	1.2	15.0	6.75	12	10	0.25	0.63	0.79	Example of present invention	
20	1.0	11.0	-	4.2	0.7	-	Si:0.1, S:0.4	17.4	Fe	12.0	1.2	12.0	6.90	16	11	0.28	0.65	0.82	Example of present invention	
21	1.0	2.6	4.3	4.4	0.3	7.2	Mn:0.3, Si:0.4, S:0.2	20.7	Fe	16.0	0.7	14.0	6.75	15	12	0.23	0.65	0.76	Example of present invention	
22	1.3	13.2	0.4	6.1	-	-	V:0.2, W:0.6, Si:0.2, S:0.5	22.5	Fe	18.0	1.2	16.0	6.80	17	9	0.25	0.62	0.75	Example of present invention	